

## ABSTRACT

Title of dissertation:

EVALUATION OF STRENGTH AND  
RELIABILITY OF SOLID-OXIDE FUEL  
CELLS AT OPERATING CONDITIONS

Patrick Stanley, Doctor of Philosophy, 2018

Dissertation directed by:

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Solid-oxide fuel cells (SOFC) have the potential to help the energy economy transition to a more efficient generation method. A challenge in SOFCs is that the composite ceramic cell must maintain a gas-tight seal between the anode and cathode while minimizing the thickness to improve performance. This seal must hold through heating and changes in oxygen content, which effect the physical and mechanical properties of the materials. To understand these effects, it is needed to investigate the effects of environment, microstructure, and macrostructure interplay on the cell's strength, modulus, and fracture toughness.

It has been a challenge to measure the mechanical properties of the materials at the conditions they are used at in SOFCs. Most research to date investigates the material properties at ambient conditions after cycling a cell or at elevated temperatures in air. As part of this work, an enclosed three point bend apparatus has been built which can be heated to the same temperature and environment as an operating SOFC, measuring their properties in-situ.

With this technique, among others, a variety of materials and systems have been characterized, including established materials, nickel-oxide and gadolinium doped ceria, to new materials such as a strontium iron cobalt molybdenum oxide. It has been determined how the choice of pore former effects the strength up to elevated temperatures, how fracture toughness and strength can increase with temperature due to relaxation of intrinsic stresses, the most likely time for failure of an SOFC is under reduction due to uniform growth of microstructure flaws and how cell orientation does not impact mechanical properties.

This new knowledge into the changing mechanical properties of the different materials and structures tested will allow for the design and optimization of SOFC devices to maximize reliability and performance. In addition, the apparatus built to measure in-situ properties can also be applied to other temperatures and gaseous environments for different applications. This work helps bring SOFCs from a theoretical lab-based technology to a reliable means of efficient energy generation for use by society.

EVALUATION OF STRENGTH AND RELIABILITY OF  
SOLID-OXIDE FUEL CELLS AT OPERATING CONDITIONS

by

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## Dedication

I dedicate this work to my wife who has supported and encouraged me throughout.

## Acknowledgments

I owe my gratitude to all the people who have made this thesis possible and because of whom my graduate experience has been one that I will cherish forever.

First and foremost I'd like to thank my advisor, Professor Rajarshi Roy for giving me an invaluable opportunity to work on challenging and extremely interesting projects over the past four years. He has always made himself available for help and advice and there has never been an occasion when I've knocked on his door and he hasn't given me time. It has been a pleasure to work with and learn from such an extraordinary individual.

Acknowledge Wachsman, George Quinn, Redox, lab-mates, AIMLab, XRCC, other specific people, family.

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## List of Abbreviations and Symbols

SOFC Solid-Oxide Fuel Cell.

# Chapter 1: Introduction

## 1.1 Solid-Oxide Fuel Cells

The world depends on fossil fuels for its daily energy needs. This is a fact that is going to stay with us for the foreseeable future. By 2040, it is estimated that fossil fuels will still supply 78% of total energy demand. [1] Traditionally, the annual increase in demand is met by an increase in supply of fuel. This increase is supplied by advances in mining and drilling operations, although recent advances have been found to be controversial, such as hydraulic fracturing. [2,3] These concerns do not even account for the increased emissions caused from combustion of fossil fuels and their effect on the global environment. [4–6]

An alternative to increasing the supply and usage of fossil fuels is to increase our efficiency of turning the fuel into useful work. Solid-oxide fuel cells (SOFCs) have the ability to solve this for applications where electrical power is desired. SOFCs allow for the direct conversion of chemical energy to electrical energy, where devices such as combustion generators must convert chemical energy to thermal energy, to mechanical energy, and finally to electrical energy. Each energy conversion has intrinsic losses, limiting efficiency. Power generation plants have efficiencies around 30%, while a stand-alone SOFC generator can convert fuel to electricity at 45 to

65% efficiency. [7, 8] SOFCs are able to run on a variety of fuel sources, such as hydrogen, methane or even biogas. [9, 10] This fuel flexibility and higher efficiency helps position SOFCs to bridge the gap in the energy economy as it transitions from fossil fuels to renewable sources.

Fuel cells operate by placing a fuel and an oxidizer (usually air) on separate sides of the cell. Ions are shuttled through the cell to react with the other species, while electrons are transported through an external circuit performing work. In the case of SOFCs, the transported ions are oxygen ions which move from the cathode to the anode through the electrolyte. Figure1.1 demonstrates how an SOFC works for a hydrogen fueled SOFC. The cathode and anode materials must facilitate the incorporation of oxygen into the cell and the reaction between the oxygen and the fuel. The cell operates at temperatures ranging from 600 °C to 1000 °C depending on the technology used in order to increase the ionic conductivity and performance. It is critical that the fuel and air remain separated by the cell. If there is a leak either through the cell or around it, then the electric potential across the cell will decrease, harming the performance.

SOFc materials rely on ionic conduction to transport oxygen from one side of the cell to the other. In ionic conduction, oxygen ions hop from site to site via oxygen vacancies, locations where an oxygen atom is missing from the lattice. Because conduction depends on vacancies, the more vacancies in the lattice, the more available sites for oxygen to move between, and the greater the conductance. The relationship between oxygen vacancy concentration and oxygen conductance is given by Equation1.1, where  $\sigma_i$  is the ionic conductivity,  $[V_O^{••}]$  is the concentration

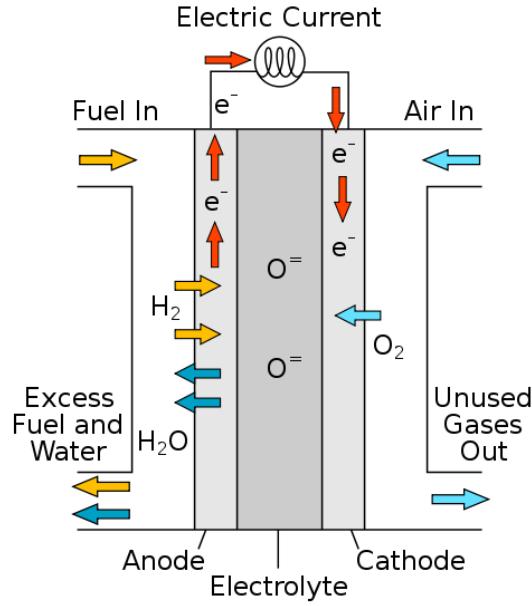


Figure 1.1: Diagram showing flow of materials in the operation of a SOFC. [11]

of oxygen vacancies in the lattice,  $\mu$  is the ionic mobility of the oxygen, and  $Ze$  is the charge of the conducting species. [12]

$$\sigma_i = [V_O^{\bullet\bullet}] Z e \mu \quad (1.1)$$

Thus by adding more oxygen vacancies to the system, the ionic conductivity increases, but changes in point defect concentrations can have other effects on the materials.

During operation, oxygen vacancies are created by exposing the anode to an environment with a low partial pressure of oxygen ( $pO_2$ ), as shown in Equation 1.2.



The oxygen on the surface of the anode side reacts with the fuel to prevent the oxygen from reincorporating into the material. The final concentration of oxygen defects will depend on the exact environmental and material conditions and location

in the cell, but some steady state value will eventually be reached. With one side of the cell exposed to low  $pO_2$ , and the other side exposed to air, a chemical potential gradient is established across the cell. This gradient drives the motion of oxygen through the cell, the oxidation of the fuel, and generates the electric current. The electrical potential at open circuit conditions is expressed by the Nernst equation, given in Equation 1.4 for the reaction given in Equation 1.3, where  $f_A$  is the fugacity of species A,  $E^o$  is the standard potential for the reaction, and n is the number of charges involved in the reaction. [13]



$$E = E^o - \frac{RT}{nF} \ln \left( \frac{f_C^c f_D^d}{f_A^a f_B^b} \right) \quad (1.4)$$

For the case of a hydrogen fueled SOFC, Equation 1.4 can be simplified to Equation 1.5. [14]

$$E = E^o + \frac{RT}{2F} \ln \left( \frac{pH_2(pO_2)^{1/2}}{pH_2O} \right) \quad (1.5)$$

From these equations it can be seen that the partial pressures of the involved species have a large role to play in the performance of the cell.

Each component of a SOFC is fabricated from a single material or from combinations of materials designed to optimize that parts function. For example, a cell can be comprised of a nickel metal-gadolinium doped ceria (GDC) anode, a GDC electrolyte, and then a lanthanum strontium manganite cathode. [15, 16] These individual components are tape cast from bulk powders, with additives such as pore formers where appropriate, into thin flexible sheets that are then laminated together and fired to create a single cell. As a result, a completed cell has distinct layers in

it where the materials and its overall properties abruptly change. This composite structure can then have inter-diffusion between layers, smoothing out the abrupt changes, but creating new structures and compositions that were not present upon lamination. [?]

Nickel has traditionally been used as an anode material in SOFCs, due to its high catalytic properties. A challenge with nickel is that at ambient conditions it oxidizes into nickel oxide, but at operating conditions it reduces to the desired nickel metal. There is a large lattice parameter change between nickel and nickel oxide, so that as it reduces, it decreases volume by over 15%. This means that the overall porosity of the anode layer increases as the SOFC is put into service. [17, 18] This increased porosity can greatly decrease the flexural strength and modulus of the anode and of the overall cell. [19, 20] The effect on flexural strength follows an exponential decay as shown in Equation 1.6, where P is the porosity, and n and  $\sigma_o$  are experimentally determined. What was once a cell that could withstand the stresses of being sealed, can weaken to the point of fracture after reduction.

$$\sigma_f = \sigma_o \exp(-nP) \quad (1.6)$$

Porosity is not a completely undesirable trait of SOFCs. For the SOFC to efficiently function, gas must be able reach the active sites in the cell. These active sites, or triple phase boundaries (TPB), are the points where gas, electronic conductor, and ionic conductor meet, as demonstrated in Figure 1.2. For example, on the anode side of a Ni-GDC cell, this would be a point where nickel meets GDC and the gas. The more TPB that are present, the more exchange can occur between the gas and

the cell. To maximize TPBs, pores can be added, greatly increasing the available surface area of the anode. Again, this becomes a trade off between added porosity for performance and a reduction in strength. [21, 22]

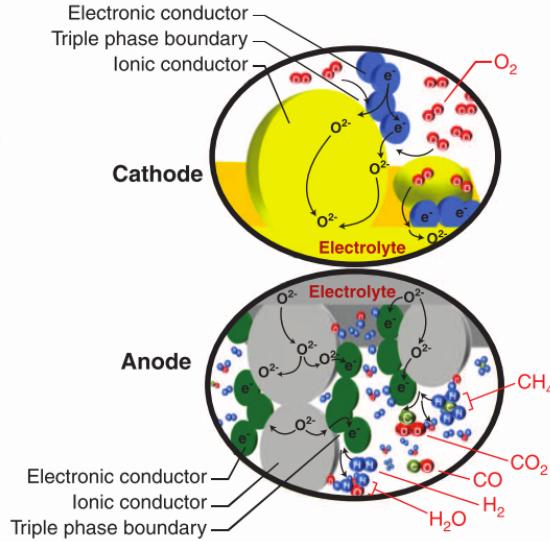


Figure 1.2: Diagram showing the triple phase boundary and the importance as being the site where incorporation and reactions occur. [7]

Ideally, a SOFC is as thin as possible to minimize diffusion path lengths and resistances in the cell. [23] Realistically, the cell must be able to withstand the stresses of being manufactured, sealed, heating, and use. This means that a compromise must be met as to how the cell is supported and which components do the supporting. Traditionally, electrolyte supported cells were used with yttria-stabilized zirconia electrolytes, but recently anode supported cells have been able to provide lower resistances while adequately supporting the cell. [24, 25] Now the anode layer, which is needed to be porous for gas diffusion, must support the majority of the stresses the cell is subjected to.

Many of the materials used in SOFC have a fluorite crystal structure, because of the crystal structure's high mobility for oxygen ions. As oxygen vacancies are produced, the interatomic bonding of the structure changes, which can change bulk properties of the crystal. [26, 27] If the strength of the atomic bonds weakens on average, due to added vacancies, it then follows that the modulus and strength of the crystal would also decrease. This relationship has been shown to fit for single grains of GDC, but this does not necessarily hold true for an actual cell. [28] Grain boundaries can play a large role in the mechanical properties of a bulk sample. For this reason microstructure combined with environmental conditions can play a large role on the overall mechanical properties of a fuel cell.

## Chapter 2: Development of Testing Apparatus

### 2.1 Overview

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## Chapter 3: Paper 1

### 3.1 Introduction

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### 3.4 Discussion

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### 3.5 Conclusions

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# Chapter 4: Defect chemistry and oxygen non-stoichiometry of double perovskite $\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_{3-\delta}$

## 4.1 Introduction

Solid-oxide fuel cells (SOFCs) are an important new technology for stationary and mobile electricity generation with no moving parts and high efficiency. SOFCs are currently limited in their application due to high operating temperatures, performance degradation due to fuel contamination, and inability to tolerate thermal and redox cycling. Creation of new materials for use in SOFCs is a main means to overcome the these limitations. To improve the performance and reliability of SOFCs the operating temperature needs to be lowered from the intermediate temperature (IT) range ( $650\text{ }^{\circ}\text{C}$  to  $800\text{ }^{\circ}\text{C}$ ) to the low temperature range ( $<650\text{ }^{\circ}\text{C}$ ). [7] Additionally, the use of an all-ceramic anode, as apposed to the traditional nickel metal anode, would improve long term performance, resistance to poisoning or coking, and better match the thermal expansion of the rest of the cell.

Perovskite structures have yielded number of mixed ionic electronic conductor (MIEC) with potential uses as SOFC anode and cathode materials. Perovskites have the structure of  $\text{ABO}_3$ , where A and B are different cation sites. This structure allows

for the stable formation of anion vacancies, allowing for oxygen conduction. [29] If multivalent metal species are used as cations, then electronic conduction can be promoted from the reduced and mixed states of the ions. [30] [31] Additionally, perovskite structures show good resistance to coking or poisoning agents and the [32]  $\text{SrMgMoO}_3$  and its related family of materials ( $\text{SrMMoO}_3$ , where M is a transition metal dopant) yield good conductivities and catalytic actives. A new composition,  $\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_{3-\delta}$ , is of particular interest because of its high conductivity ( $\sim 35 \text{ S/cm}$ ) and stability. [33–35] Possible application of MIEC materials, and thus SFCM, include electrodes for SOFC and other devices, chemical sensors or catalysts. [36]

Conduction can occur through the material in either ionic or electronic species. The total conductivity,  $\sigma_t$  is the sum of all conducting species. In the case of Equation 4.1 it is the sum of the electronic conductivity,  $\sigma_e$ , and ionic conductivity,  $\sigma_i$ . Electronic conductivity in turn is the sum of the conductivity due to the electrons or holes and is given by Equation 4.2, where  $e$  is the fundamental charge of an electron,  $\mu$  is the mobility of a species, and  $n$  is the concentration of electrons while  $p$  is the concentration of holes. Ionic conductivity occurs in this case by transportation of oxygen through vacancy sites and is given by Equation 4.3, where  $Z$  is the number of charges for the species, and  $[\text{V}_\text{O}^{\bullet\bullet}]$  is the concentration of oxygen vacancies using Kröger–Vink notation. Oxygen vacancies and electronic species are affected by the partial pressure of oxygen in the environment. The material can respond by either electronic compensation, Equation 4.4, generating electrons and vacancies as oxygen leaves the material, or ionic compensation, Equation 4.5, where a metal cation,  $M$ ,

reduces with the creation of a vacancy. The balance between ionic and electronic compensation depends on the free energies of reactions for all possible reactions and the environmental conditions, but plays a direct role in the conductivity and non-stoichiometry of the material.

$$\sigma_t = \sigma_e + \sigma_i \quad (4.1)$$

$$\sigma_e = e\mu_n n + e\mu_p p \quad (4.2)$$

$$\sigma_i = Ze\mu_i[V_O^{\bullet\bullet}] \quad (4.3)$$



In this work the oxygen non-stoichiometry and conductivity of SFCM has been measured to better understand the defect structure of the material. The non-stoichiometry of SFCM was measured under oxidizing and reducing environments similar to LT-SOFCs using thermogravimetry. Temperature programmed desorption spectroscopy characterized at what temperatures the maximum oxygen loss is observed. A defect equilibrium model and diagram is proposed from non-stoichiometry and conductivity data and results are compared to other perovskite materials.

## 4.2 Experimental

### 4.2.1 Sample Preparation

SFCM was created from stoichiometric amounts of strontium carbonate ( $SrCO_3$ , Sigma-Aldrich), iron oxide ( $Fe_2O_3$ , Sigma-Aldrich), cobalt oxide ( $Co_2O_3$ , Infram

Advanced Materials), and molybdenum oxide ( $\text{MoO}_3$ , Alfa-Aesar) using conventional solid-state methods. The constituents were ball milled for 24 hours in ethanol and dried using a 100 °C oven. Afterwards the powder was calcined at 1100 °C for four hours.

Dense SFCM bars were used to maximize the total mass and mass changes during testing. Samples were made by combining SFCM powder with 0.6 wt% polyethylene glycol 600, 1.8 wt% ethylene glycol, and 0.6 wt% glycerol in isopropyl alcohol and ball milling overnight. After drying at 100 °C, the powder was ground by mortar and pestle, then pressed uniaxially into rectangular bars at 1 metric ton and isostatically pressed at 6 metric tons. Bars were sintered by heating to 400 °C for one hour and then 1340 °C for four hours, using a  $3 \text{ }^\circ\text{C min}^{-1}$  heating and cooling rate. This produced bars with 97% theoretical density.

#### 4.2.2 X-ray Diffraction

X-ray diffraction (XRD) was used to confirm phase purity of the SFCM after synthesis and during the testing process. A Bruker D8 Advance with LynxEye was used with a  $\text{Cu K}_\alpha$  source. A step size of 0.02° was used with a dwell of 0.8 s was used.

#### 4.2.3 Conductivity

Total conductivity was measured using the four-wire technique and a Stanford SR 830 lock-in amplifier. A bar shape sample was used with dimensions of

6.46 mm × 3.3 mm × 1.3 mm. Gold paste was used as a current collector. The current range was between 0.005 to 0.05 A. A YSZ oxygen sensor was used to monitor the changes in oxygen partial pressures.

#### 4.2.4 Thermogravimetric Analysis (TGA)

Changes in mass of SFCM were measured by a Cahn D200 microbalance with the sample suspended down a quartz tube into a furnace. The furnace used to heat the sample was located outside the quartz tube and was controlled by a PID controller with a K-type thermocouple placed immediately below the sample inside the quartz tube. Gas flow was controlled at consistent 50 sccm by mass flow controllers, which mixed dry nitrogen, oxygen, humidified nitrogen and hydrogen to obtain the  $p_{O_2}$  desired. Measurements of the  $p_{O_2}$  were taken by a calibrated yttria-stabilized zirconia (YSZ) oxygen sensor located before the sample.

To prepare the sample it was pre-weighed, wrapped in platinum wire and suspended from the balance, placed in the furnace with simulated air (21% O<sub>2</sub>, 79% N<sub>2</sub>) flowing. Once the mass had stabilized, the furnace was heated to 800 °C to allow for any organic contamination to burn off. After the mass stabilized at this elevated temperature the sample could be introduced to various environments. The mass of the sample would be noted only after steady state had been reached. After testing a sample, a bar of alumina was cut to the same dimensions as the sample and the process was repeated to obtain a blank which could be subtracted from the measurements to remove any buoyancy effects.

Oxygen non-stoichiometry was calculated using Equation 4.6, where  $\Delta\delta$  is the change in oxygen stoichiometry,  $MW_{SFCM}$  is the molecular weight of SFCM ( $208.74 \text{ g mol}^{-1}$ ),  $MW_O$  is the molecular weight of oxygen ( $16.0 \text{ g mol}^{-1}$ ),  $w_{sample}$  is the weight of the sample, and  $\Delta w$  is the weight change as recorded by the TGA. The oxygen vacancy concentration is calculated using Equation 4.7, where  $V_{unitcell}$  is the volume of a SFCM unit cell and  $N_A$  is Avogadro's number. To calculate the absolute oxygen vacancy concentration, the non-stoichiometry of SFCM at a point needs to be known. For this work, it is assumed that in a pure oxygen environment all oxygen vacancies are filled with no oxygen interstitial or surface species, thus  $\delta = 0$ .

$$\Delta\delta = \frac{MW_{SFCM}}{MW_O w_{sample}} \Delta w \quad (4.6)$$

$$[V_O^{\bullet\bullet}] = \frac{\delta\rho}{MW_{SFCM}} \quad (4.7)$$

#### 4.2.5 Temperature Programmed Desorption

The effluent from the TGA was used as the inlet to a mass spectrometer (MS) to perform temperature programmed desorption. The sample was prepared as before and heat treated to remove any carbon contaminants, but was allowed to cool under simulated air. It was then heated to  $800^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$  under a flow of nitrogen as the MS measured the  $32 \text{ m/z}$  signal which corresponded to  $\text{O}_2$  desorption. Additional  $\text{m/z}$  signals were monitored to observed for other species.

### 4.3 Results and Discussion

Throughout the reduction and oxidation treatments performed on SFCM, the material remained pure phase. A theoretical XRD pattern was obtained by calculating a pattern from the ordered double perovskite structure of SMMO and doping Fe to all B-sites randomly. Figure 4.1a has the XRD patterns of SFCM after synthesis and after reduction and oxidation treatments. The ordered double perovskite unit cell is presented next to it, which was used to create the theoretical XRD pattern in Figure 4.1b. [37] Within the tested environment range (up to 650 °C and  $p_{O_2}$  from 1 to  $10^{-24}$  atm)

Small changes can be seen to occur in the XRD pattern after different treatments. These are accounted for by the differences in oxidation state, vacancy concentration, and thus lattice parameter left in the sample after reduction or oxidation.

SFCM has a conductivity typical of other MIEC conductors, as shown in Figure 4.2. At high  $p_{O_2}$  ranges ( $10^{-1.5}$  atm to 1 atm) shows p-type conductivity, increasing conductivity with  $p_{O_2}$ . Down to  $10^{-1}$  atm the change in conductivity is linear with a slope of 0.089 (log-log scale). Below  $10^{-1}$  atm the slope changes away from the previous trend. At low  $p_{O_2}$  ranges ( $10^{-24}$  atm to  $10^{-19}$  atm) the conductivity behaves linearly with n-type conductivity, increasing at lower  $p_{O_2}$  with a slope of -0.11 (log-log scale).

To confirm that oxygen desorption occurs to SFCM when heated under reducing conditions, TPD was performed in conjunction with TGA. Figure 4.3 presents the data from the TGA on top with the mass and rate of mass change while the 16 m/z

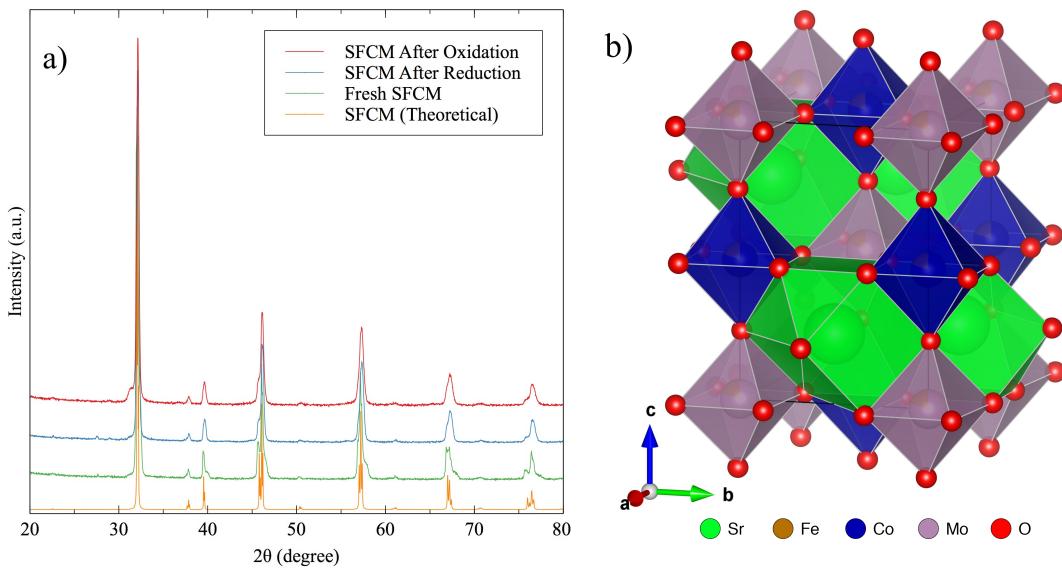


Figure 4.1: a) Powder XRD patterns of SFCM samples taken after synthesis, reduction, and oxidation compared to a theoretical SFCM diffraction pattern. b) Crystal structure of theoretical, ordered double perovskite SFCM.

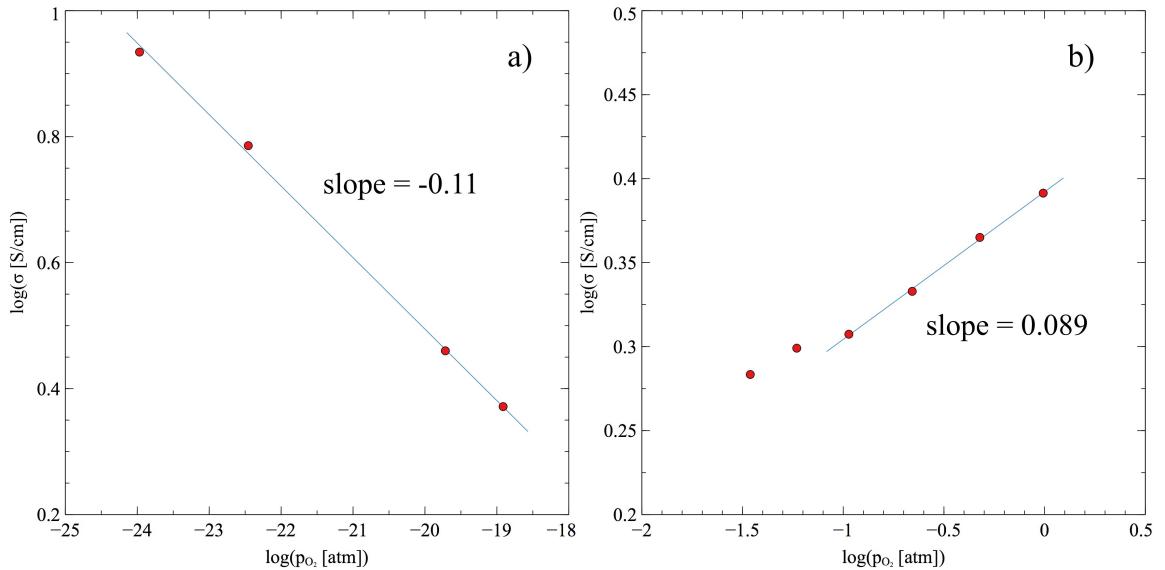


Figure 4.2: Total conductivity as the environment changes oxygen content at 600 °C.

signal from oxygen in the mass spectrometer is on bottom. Both mass and MS signals contain noise from the PID control on the furnace. The rate of mass loss matches the oxygen signal from the MS, confirming that oxygen is generated from SFCM when heated under reducing conditions and is the cause for mass loss in the sample. SFCM shows two maxima for the rate of oxygen loss during heating. The first,  $\alpha$ , occurs at 405 °C with the second peak,  $\beta$ , occurring near 800 °C.

Oxygen non-stoichiometry and oxygen vacancy concentrations are shown in Figure 4.4 at 600 °C for high and low  $p_{O_2}$  regions. At high  $p_{O_2}$  SFCM has two linear regions, changing between them near  $10^{-0.75}$  atm. The transition between regions in oxygen stoichiometry occurs at a similar  $p_{O_2}$  where the conductivity changes in Figure 4.2. In the high  $p_{O_2}$  region, a linear trend occurs down until  $10^{-21}$  atm where the non-stoichiometry increases.

TGA non-stoichiometry measurements were also performed at 400 °C and 500 °C which are temperatures in the LT-SOFC range. Figure 4.6 shows the non-stoichiometry measurements for the sample tested at three temperatures in the low  $p_{O_2}$  (a) and high  $p_{O_2}$  (b) regions. As expected lowering the temperature reduces the non-stoichiometry at a given  $p_{O_2}$  and decreases the  $p_{O_2}$  at which transitions occur between regimes.

Using the collected data with Equations 4.1–4.5, a general defect diagram can be made. While the exact concentrations of defects is not presented, the general trend and relative concentrations hold true.

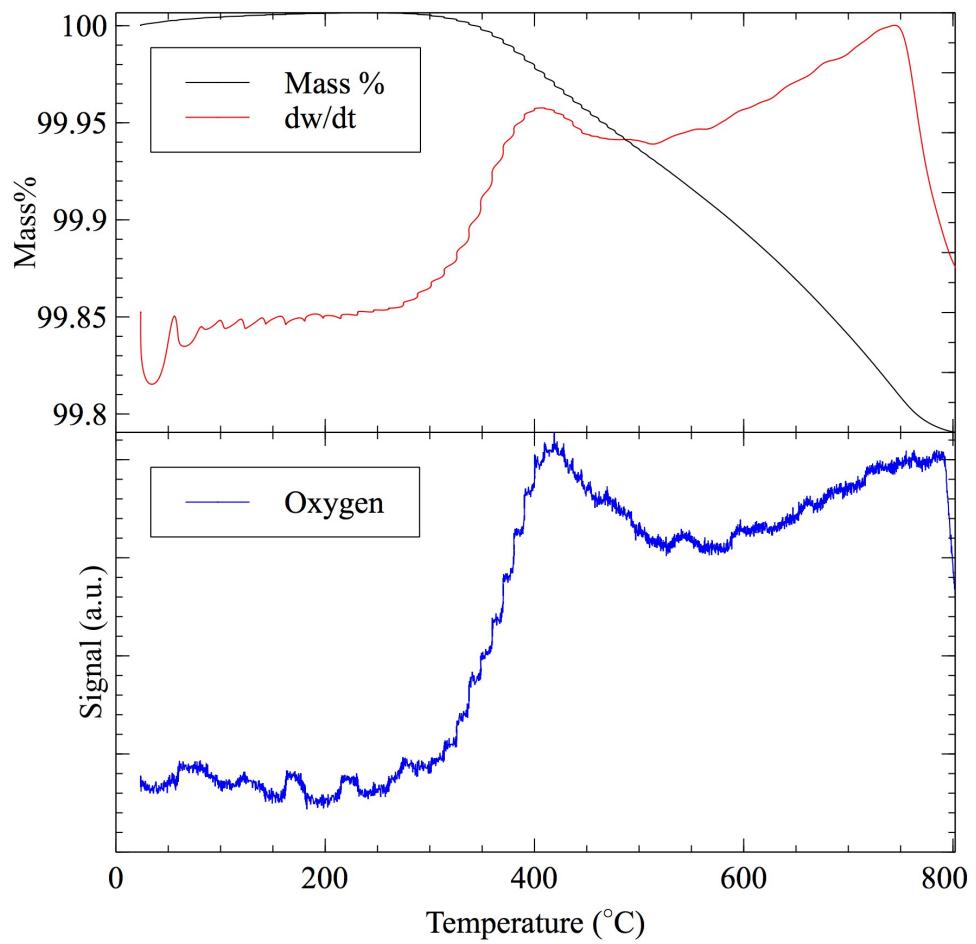


Figure 4.3: Temperature programmed desorption of oxygen in SFCM with mass loss from TGA (top) and oxygen desorption from MS (bottom) as it is heated to 800 °C in N<sub>2</sub>.

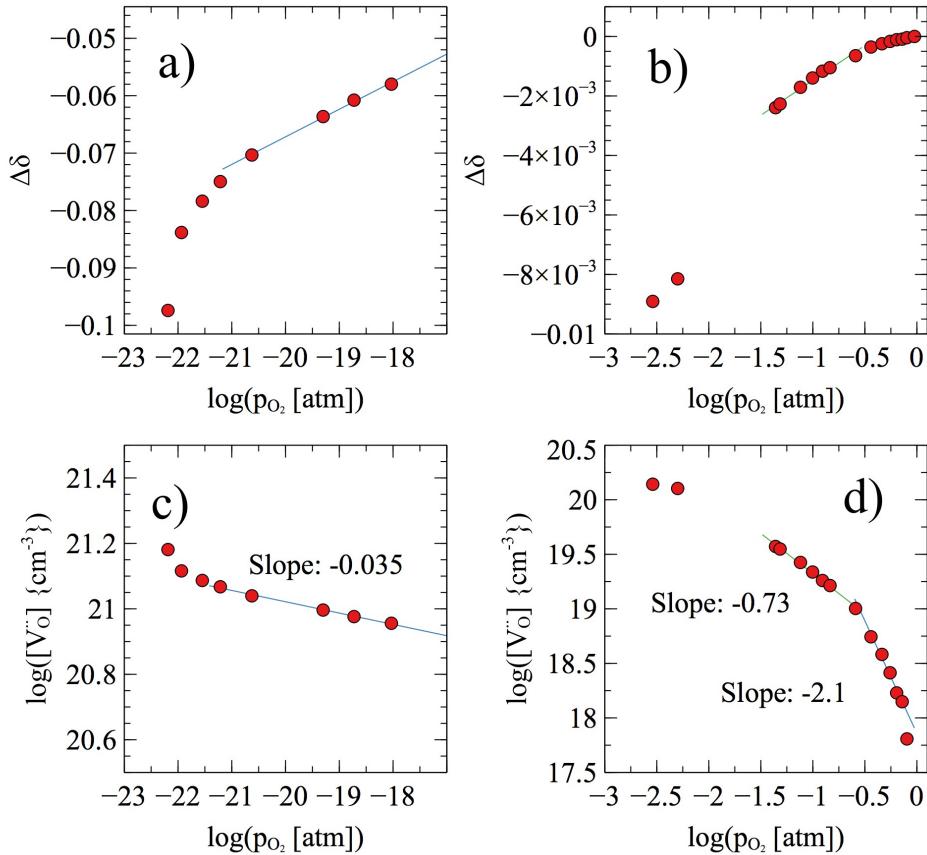


Figure 4.4: Non-stoichiometry (top) and corresponding oxygen vacancy concentration (bottom) of SFCM under oxidizing conditions (right) and reducing conditions (left) at 600 °C.

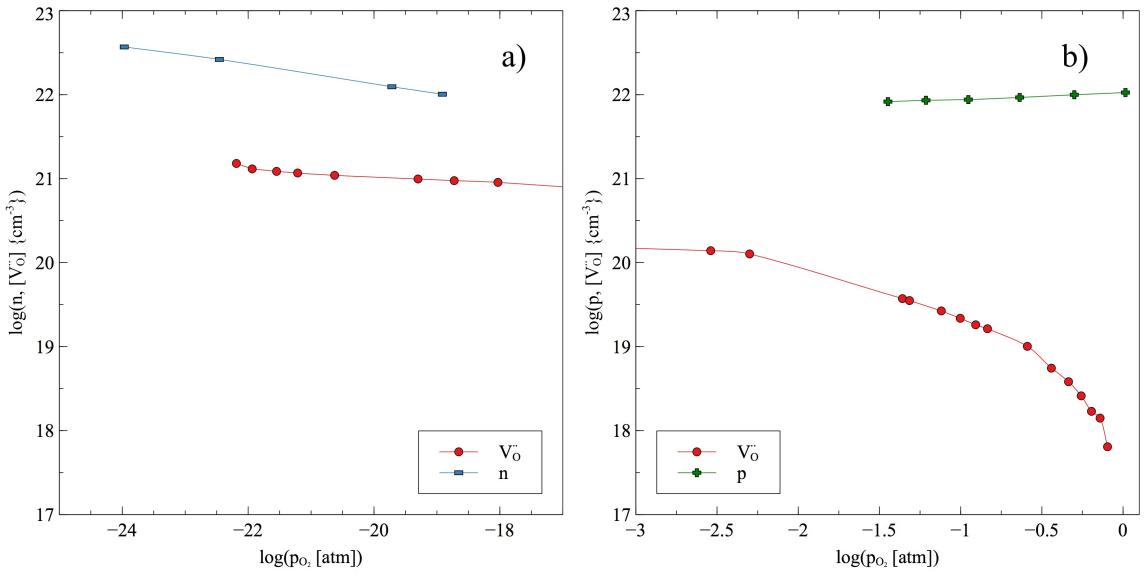


Figure 4.5: Oxygen vacancy and electronic defects in SFCM based on conductivity and TGA non-stoichiometry.

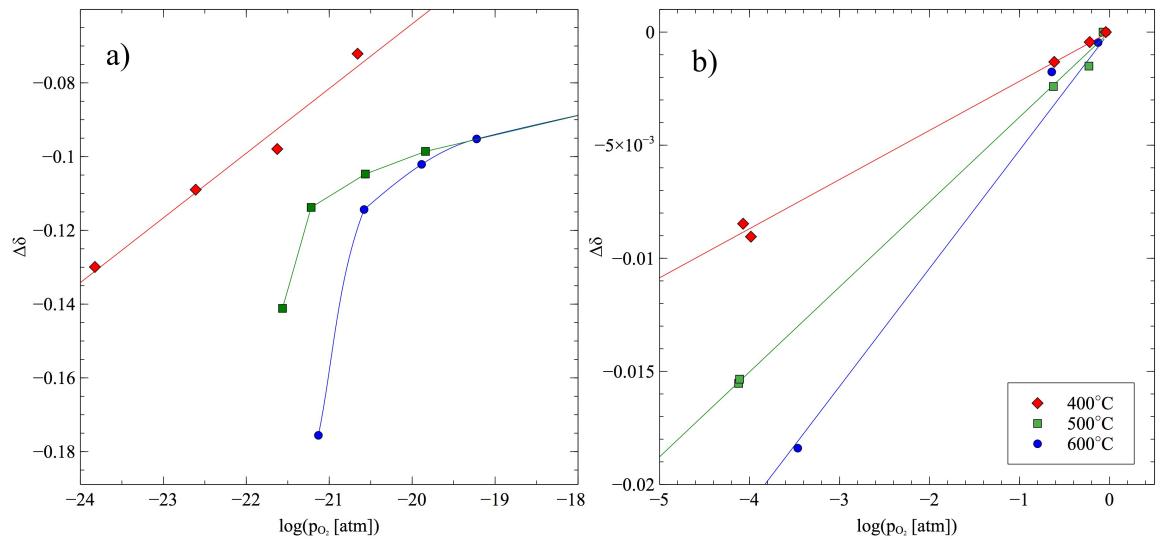


Figure 4.6: Non-stoichiometry of SFCM as  $p_{O_2}$  changes at 400 °C, 500 °C, and 600 °C.

## 4.4 Conclusions

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Chapter 5: Flexural strength and flaw distributions of  $\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_3$   
based ceramic-supports for solid-oxide fuel cells at operating conditions

## 5.1 Introduction

New materials are regularly being developed for use in solid-oxide fuel cells (SOFCs) to lower operating temperatures and improve reliability and performance.

[7] Most of the development focuses on the catalytic activity and conductivity enhancement in the material. However, an important characteristic of these materials that needs to be studied are the mechanical properties. An SOFC must be able to be adequately compressed to create a gas tight seal between the anode and cathode compartments for it to function well. This means that the cell must withstand the induced stresses from sealing, heating, and reduction by fuels. Redox cycling presents an additional challenge, especially in nickel-based systems, because oxidation and reduction phase changes cause crack growth and failure after a few cycles.

[18, 21, 22, 38–41] A means of mitigating this problem is to use alternative, all ceramic anode system, such as  $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_3$ ,  $\text{Sr}_{0.94}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_{3-\delta}$ ,  $\text{Ba}_{0.98}\text{La}_{0.02}\text{SnO}_3$ , or  $\text{Sr}_2\text{MgMoO}_6$  (SMMO). [30, 31, 42–46]

One new material of interest is the double perovskite  $\text{SrFe}_{0.2}\text{Co}_{0.4}\text{Mo}_{0.4}\text{O}_3$  (SFCM). [33–35] SFCM is a mixed ionic electronic conductor (MIEC) based off SMMO and other similarly structured anodes. The double perovskite family of materials, similar to SFCM and SMMO, have potential use as SOFC components due to the ability of the stable perovskite structure to generate and conduct oxygen vacancies and the multivalent cations allowing for electronic conduction and catalytic activity. [29, 47, 48] A similar thermal expansion of SFCM to GDC increases the compatibility between the components and reduces the chances of cracking and cell failure. SFCM has a high conductivity of  $\sim 35 \text{ S/cm}$  at  $650^\circ\text{C}$  and is stable to redox cycling making it a promising material.

As an SOFC cell is heated and reduced, there is the possibility for changes to occur in the fracture toughness or flaw distribution of the materials. Heating causes the materials to expand, increasing their interatomic distances, and reduction creates oxygen vacancies weakening bonds. [49, 50] Flaws can grow, combine, or change shape during these processes further affecting the overall strength. Equation 5.1 demonstrates how various factors impact the strength of a sample, where  $\sigma$  is the strength,  $K_{Ic}$  is the fracture toughness,  $Y$  is the shape factor for the flaw which caused failure and  $a$  is the size of the flaw. [51] The fracture toughness and flaw distributions play a direct role in the overall strength of the cell.

$$\sigma = \frac{K_{Ic}}{Y\sqrt{a}} \quad (5.1)$$

Most research focuses on measuring and comparing the Young's moduli of different materials as it changes with environment. [17, 52–54] While the modulus

can be correlated to the fracture strength of the cell, direct measurement of flexural strength remains the best means to characterize the strength of the cell. This work characterizes the changes which occur in fracture toughness and flaw distributions of SFCM, SFCM-GDC anode support layer (ASL), and SFCM-GDC/GDC half-cells when exposed to oxidizing and reducing conditions up to 600 °C by use of flexural testing and Weibull analysis. Additionally, electrical conductivity, thermogravimetric analysis, and thermal expansion are used to determine the causes for changes in mechanical properties under these conditions.

## 5.2 Experimental

### 5.2.1 Sample Preparation

SFCM powder was synthesized with conventional solid-state methods using stoichiometric amounts of strontium carbonate ( $\text{SrCO}_3$ , Sigma-Aldrich), iron oxide ( $\text{Fe}_2\text{O}_3$ , Sigma-Aldrich), cobalt oxide ( $\text{Co}_2\text{O}_3$ , Inframat Advanced Materials), and molybdenum oxide ( $\text{MoO}_3$ , Alfa-Aesar). The components were ball milled in ethanol for 24 hours, dried at 100 °C, and heated to 1100 °C for four hours.

To create fracture toughness test samples, SFCM powder was ball milled overnight with a mixture of 0.6 wt% polyethylene glycol 600, 1.8 wt% ethylene glycol, and 0.6 wt% glycerol in isopropyl alcohol. It was then dried at 100 °C, ground by mortar and pestle, pressed uniaxially into rectangular bars at 30 MPa, then isostatically pressed at 30 MPa. Sintering followed by heating to 1340 °C for four hours at 3 °C/min with a one hour hold at 400 °C to allow the binders to burn

out. This process achieved dense samples at 97% average theoretical density with no apparent flaws in the bars. Bars were then cut and sanded to final dimensions of 3 mm x 4 mm x 25 mm. The chevron notch was cut using the jig described by Jenkins, Chang and Okura following the ASTM procedure. [55, 56]

Tape casting was used to create test coupons of porous SFCM-GDC ASL and half-cells. Using ethanol as a solvent, SFCM-GDC was ball milled with polyvinyl butyral, benzyl butyl phthalate, 12  $\mu\text{m}$  poly(methyl methacrylate) (16 wt% with respect to SFCM-GDC), and Menhaden fish oil. The tape was cast to a thickness of 110  $\mu\text{m}$  on Mylar then laminated using a hot press to a final thickness of 660  $\mu\text{m}$ . Dense GDC was casted to 30  $\mu\text{m}$  and laminated to the top of the SFCM-GDC to create half-cells. Individual coupons were cut from the green tape, sintered at 1200 °C for four hours, with holds at low temperatures to burn out organic binder and pore former. The final thicknesses were measured to be 400  $\mu\text{m}$  for the SFCM-GDC ASL and  $\sim$ 20  $\mu\text{m}$  thick GDC electrolyte. Test coupons had their edges sanded to remove defects left from cutting, following ASTM standards. [57] Top and bottom surfaces were not sanded to preserve possible defects left from tape casting procedure, which would be representative of industrially manufactured SOFCs.

X-ray diffraction (XRD) was used to check and confirm phase purity of SFCM samples throughout the preparation and testing process. A Bruker D8 Advance with LynxEye was used with a Cu K $\alpha$  source. A step size of 0.02° was used with a dwell of 0.8 s to obtain diffraction patterns.

### 5.2.2 Conductivity

Direct current conductivity was measured using rectangular bars of SFCM and SFCM-GDC (2:1) composite. The samples were connected to a Keithley 2400 source meter by silver paste and wire. Using an in-house built reactor, the sample could be heated and the gas environment could be controlled. An initial measurement was taken after heating and 50 hours of exposure to 10% H<sub>2</sub> in N<sub>2</sub>, then the sample exposed cycled between air and reducing conditions over a period of 14 days.

### 5.2.3 Thermogravimetric Analysis (TGA)

Mass of samples during oxidation and reduction cycling was measured using a Cahn D200 microbalance. The samples were placed in a crucible suspended from a platinum wire attached to the microbalance and enclosed by an alumina tube inside a furnace. Heating control was achieved with a PID loop and temperature measurement done by a K-type thermocouple placed immediately below the sample inside the alumina tube. Gas flow was controlled at a constant 50 sccm by mass flow controllers. 21% O<sub>2</sub> in dry N<sub>2</sub> was used for the oxidizing condition while 3% H<sub>2</sub> in N<sub>2</sub> humidified with 3% H<sub>2</sub>O was used for the reducing conditions.

### 5.2.4 Mechanical Measurements

Measurements of mechanical properties were collected using a Tinius Olsen 10ST Universal Testing Machine equipped with a 250 N load cell. Experiments where any samples would be tested at elevated temperatures or under reducing

environments were conducted using a custom built three point flexural test fixture placed inside a gas-tight chamber and furnace. Otherwise, a fully-articulating four point flexural test fixture was used. Samples tested at ambient conditions were placed on the appropriate testing fixture and loaded until failure. For samples tested at elevated temperatures the sample was heated in the test chamber at  $10\text{ }^{\circ}\text{C min}^{-1}$ , allowed to equilibrate for 20 minutes, then tested. Samples to be reduced were placed in the chamber, heated and exposed to reducing gas for 18 hours before being tested.

#### 5.2.4.1 Flexural Strength

A loading rate of 0.2 mm/min was used for all strength measurements. Strength was calculated from the maximum force measured before failure according to Equation 5.2 or 5.3 depending on if the four point or three point fixture is used respectively, where  $\sigma$  is the strength,  $P$  is the maximum force,  $L$  is the span width of the test fixture,  $b$  is the width of the sample and  $d$  is the thickness of the sample. Equation 5.2 is for a fixture where the top span is 1/2 the width of the bottom span. [57]

$$\sigma = \frac{3PL}{4bd^2} \quad (5.2)$$

$$\sigma = \frac{3PL}{2bd^2} \quad (5.3)$$

#### 5.2.4.2 Chevron Notch Fracture Toughness

The fracture toughness of chevron notched samples were measured using a loading rate of 0.001 mm/min. Fracture toughness was calculated from the maximum force using Equation 5.4 or 5.5 for four point or three point fixtures. [56, 58]  $Y_{min}^*$  is

the shape factor as calculated by Equation 5.6,  $S_o$  and  $S_i$  are the outer and inner spans,  $B$  is the width of the sample,  $W$  is the height of the sample,  $a_0$  is the distance from the tip of the chevron notch to the bottom of the sample, and  $a_1$  is the average distance from the side of the chevron notch to the bottom of the sample. Each sample was measured after failure, but in this study the approximate values were  $S_o = 40mm$ ,  $S_i = 20mm$ ,  $B = 3.0mm$ ,  $W = 4.0mm$ ,  $a_0 = 0.80mm$ ,  $a_1 = 3.8mm$ . Fracture toughness was measured only under air at room temperature and up to 600 °C. Under reduction the fracture toughness bars would spontaneously fracture, preventing measurements under that condition.

$$K_{Ivb} = Y_{min}^* \left[ \frac{P[S_o - S_i]}{BW^{3/2}} \right] 10^{-6} \quad (5.4)$$

$$K_{Ivb} = Y_{min}^* \left[ \frac{P}{BW^{1/2}} \right] 10^{-6} \quad (5.5)$$

$$Y_{min}^* = \frac{0.38742 - 3.0919(a_0/W) + 4.2017(a_1/W) - 2.3127(a_1/W)^2 + 0.6379(a_1/W)^3}{1.0000 - 2.9686(a_0/W) + 3.5056(a_0/W)^2 - 2.1374(a_0/W)^3 + 0.0130(a_1/W)} \quad (5.6)$$

### 5.3 Results and Discussion

#### 5.3.1 Redox Cycling Stability

SFCM has a high initial conductivity of 35 S/cm but decreases after 3 cycles to 19 S/cm and again at 9 cycles, shown in Figure 5.1a. The addition of GDC to create a SFCM-GDC composite decreases the initial conductivity to 15 S/cm. At 4 cycles, SFCM-GDC decreases conductivity and stabilizes to 8 S/cm for 19 cycles. The addition of the GDC improved the redox cycling stability by providing a very

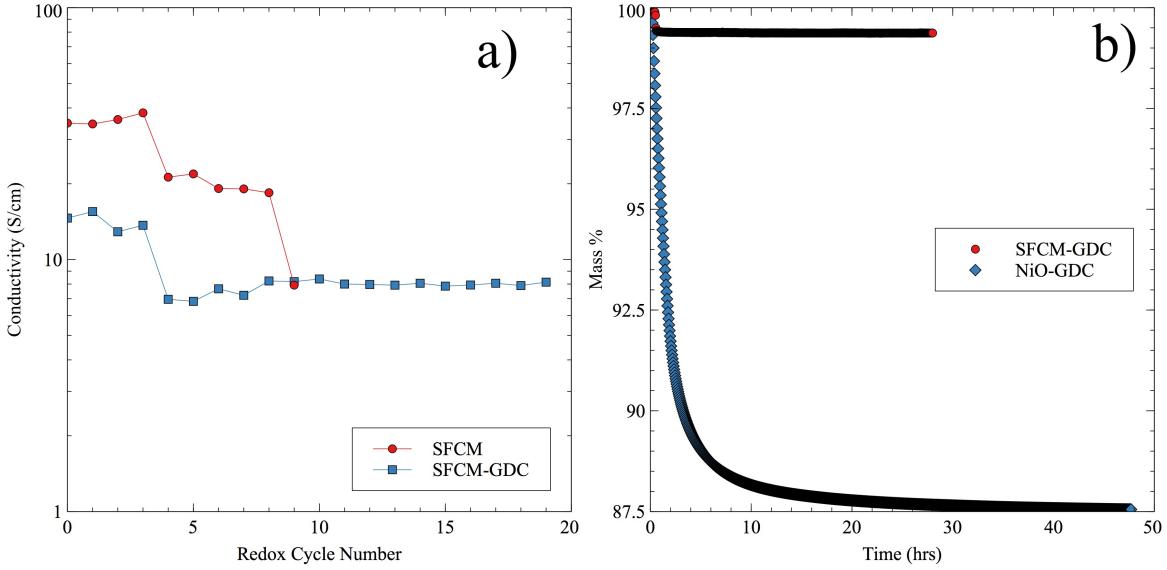


Figure 5.1: a) DC conductivity of SFCM and SFCM-GDC after cycling at 650 °C between 10% H<sub>2</sub> in N<sub>2</sub> and air. b) Mass loss of SFCM-GDC and NiO-GDC during reduction in 3% H<sub>2</sub>/3% H<sub>2</sub>O in N<sub>2</sub> at 650 °C.

stable, contiguous framework for the SFCM. [12, 27, 50]

Figure 5.1b shows the mass loss of SFCM-GDC as it is reduced in 3% humidified H<sub>2</sub>. For comparison, another popular anode material, nickel oxide GDC, is plotted along with it. The reduction of SFCM-GDC results in a less than 1% reduction of mass from the formation of oxygen vacancies in the SFCM and GDC, and it reaches steady state in under two hours. NiO-GDC on the other hand loses a large amount of mass from the reduction and phase change of NiO to Ni metal taking over 30 hours to reach steady state.

Further cycling of SFCM in the thermogravimetric analyzer (TGA) was performed and results are given in Figure 5.2 with 5.2a showing the mass loss of SFCM with time as it is cycled between air and hydrogen and 5.2b being a summary of the

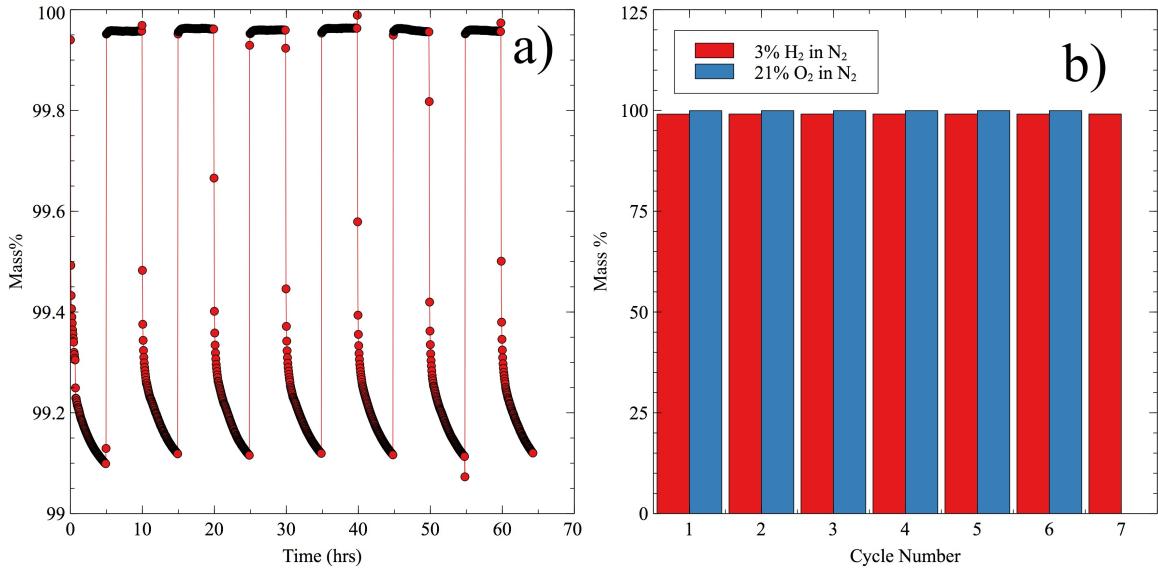


Figure 5.2: Mass changes of SFCM during cycling between 21% O<sub>2</sub> and 3% H<sub>2</sub>/3% H<sub>2</sub>O in N<sub>2</sub> at 600 °C. Each exposure was 5 hours. a) Percent mass change with time as the gas is switched back and forth. b) Summary of maximum and minimum changes with each cycle.

total mass changes that occur with each cycle. With each cycle, less than 1% total mass change is observed. Reduction occurs over a time period of five hours while oxidation happens at a faster rate, approximately one hour. Fitting the reduction and oxidation to exponential functions gives a biexponential with decay rates of 0.438 and 27.89 for reduction and an oxidation rate of 2.90. This demonstrates that SFCM does not generate any additional phases which cause the loss or gain of oxygen and that reduction and oxidation are reversible processes which occur over short periods.

### 5.3.2 Fracture Toughness

Fracture toughness was found to be  $(0.124 \pm 0.023) \text{ MPa}\sqrt{\text{m}}$  at room temperature, increasing with temperature up to  $600^\circ\text{C}$ , as shown in Figure 5.3a. From room temperature to  $500^\circ\text{C}$ , the rate of increase in  $K_{\text{Ic}}$  is low at  $4.3 \times 10^{-5} \text{ MPa}\sqrt{\text{m}}/\text{°C}$ . From  $500^\circ\text{C}$  to  $600^\circ\text{C}$  the fracture toughness increases by 90%. The increase in fracture toughness is a result of the thermal expansion of the material. During process of creating the bar, the sample was cooled from  $1340^\circ\text{C}$  to room temperature. This cooling and associated contraction induces stresses in the bar sample, which combine with the stresses added during testing to fracture the sample. As the sample is heated, the residual stresses are relaxed, increasing the amount of stress which must be applied externally to cause the bar to fracture. Any change in fracture toughness due to the weakening of bonds is masked by this effect. The increase in fracture toughness from  $500^\circ\text{C}$  to  $600^\circ\text{C}$  matches the temperature where the rate of thermal expansion also increases, as shown in Figure 5.3b.

Figure 5.3b also presents the thermal expansion of GDC and a SFCM-GDC composite. At temperatures below  $550^\circ\text{C}$  the expansion of SFCM-GDC matches that of pure SFCM, greater than that of pure GDC. Above  $550^\circ\text{C}$ , the rate of expansion slows in comparison to SFCM and matches the rate of expansion for GDC. Thus, below  $550^\circ\text{C}$ , SFCM-GDC expands the same as SFCM and above  $550^\circ\text{C}$  it expands the same as GDC. We would then expect that SFCM-GDC composites have the same increase in fracture toughness as SFCM up to  $550^\circ\text{C}$  due expansion and relaxation of intrinsic stresses, but not further increase the rate above  $500^\circ\text{C}$ , as SFCM does.

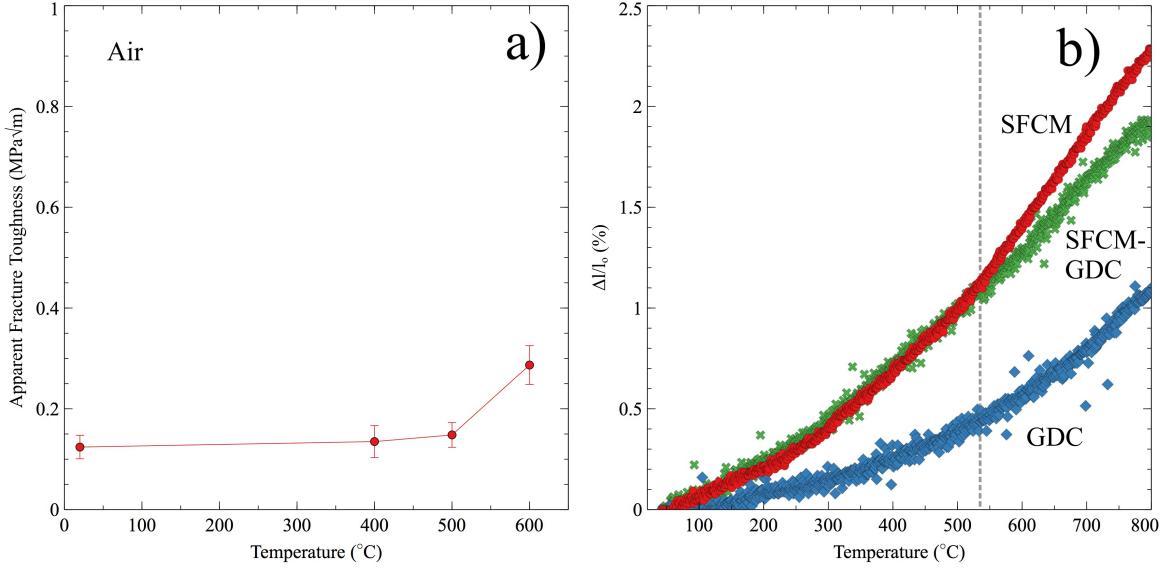


Figure 5.3: a) Fracture toughness of SFCM from 20 °C to 600 °C. b) Thermal expansion of SFCM, GDC, and SFCM-GDC.

### 5.3.3 Half-cell Strength of Anode-Supported SOFCs at Operating Conditions

Figure 5.4 gives box plots of the results of three point flexural testing of SFCM-GDC/GDC half-cells, and Table 5.1 summaries the strengths. The circles on the right of 5.4 represent the results of a Student's t-test, to determine if the means of the different data sets are the same. The more the circles overlap the more similar the data sets are. In this case, there is no overlap between circles at the 95% confidence interval, highlighting that the strengths tested at each condition are unique from each other.

At ambient conditions the strength of the half-cells was measured to be 57.7 MPa. Upon heating, the strength increases to 74.2 MPa. This result corre-

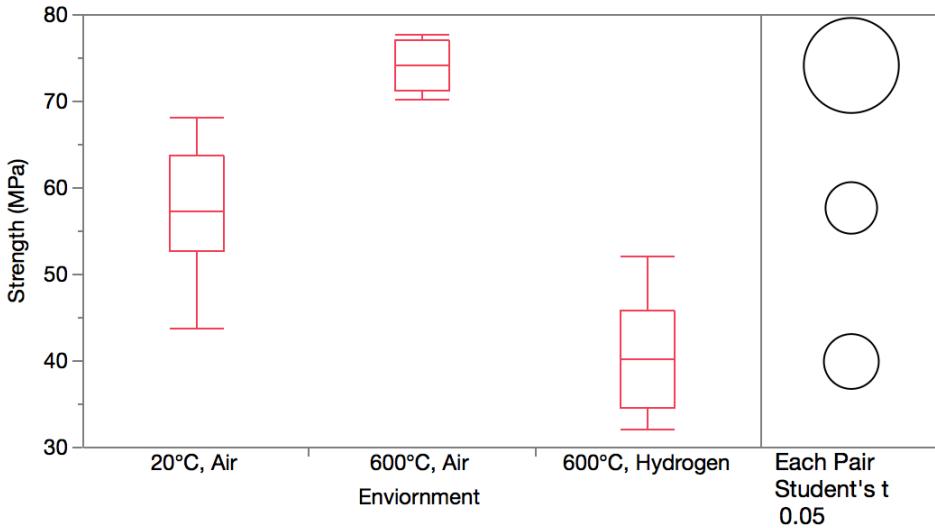


Figure 5.4: Flexural strengths of half-cell coupons made from SFCM-GDC anode with GDC electrolyte tested at 20 °C in air, 600 °C in air, and 600 °C in 5% H<sub>2</sub>.

lates with the increase in fracture toughness discussed earlier, which is expected based on Equation 5.1. Another contributing factor to the increase in strength is the effect thermal expansion has on pre-existing cracks and flaws. Any expansion of the material helps push closed a surface crack which would lead to failure, decreasing its size and increasing the stress that would be required to cause that crack to open and propagate.

Upon reduction of the half-cell at 600 °C, the fracture strength decreases, below that of the ambient strength, to 39.9 MPa. This reduction of strength is likely due to the combination of the decrease in fracture toughness and the growth of microcracks as the materials reduce in volume.

Weibull analysis was performed to compare the distribution of flaws between the ambient tested half-cells and the in-situ reduced half-cells. Figure 5.5 displays

Table 5.1: Summary of strengths for SFCM-GDC/GDC half-cells at different environments

Temperature (°C)	Atmosphere	Number	Mean (MPa)	Std Dev (MPa)
20	Air	17	57.7	6.71
600	Air	5	74.2	2.98
600	5% H <sub>2</sub>	14	39.9	5.89

the fitting of Weibull distributions to the flexural strength of half-cell coupons tested at ambient conditions and during reduction at 600 °C. Table 5.2 summarizes the fitting parameter for the Weibull modulus with 95% confidence intervals using the maximum-likelihood method. Between the two conditions, there is an appreciable change in the Weibull modulus of the two samples. The Weibull modulus increases decreases from 10.4 at ambient conditions to 7.29 when at reducing conditions. This indicates that the distribution of flaws has changed by becoming wider, creating more variability between flaws. It is possible that this change is the result of an uneven growth of two different flaw types.

To confirm this, fractography would need to be performed on every sample, identifying the flaw, but this is not possible due to the porous nature of the fracture surface which obscures the fracture origin. Scanning electron microscopy was performed on fracture surfaces and epoxy filled samples from each condition to look for any microstructural changes. Figure 5.6 shows the epoxy filled and polished samples with no discernible difference between samples. No difference is observed because

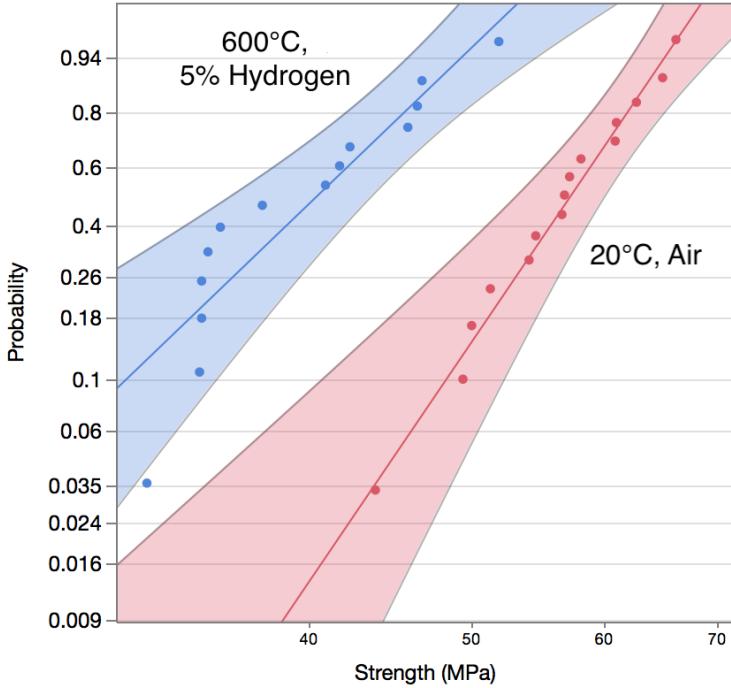


Figure 5.5: Fitted Weibull distributions of SFCM-GDC/GDC half-cells at different environments, plotted linearly with 95% confidence intervals shaded.

the likely cause of failure, microcracks, would exist along grain boundaries and are obscured by the grain boundaries and pores. [18, 59]

### 5.3.4 Strength of Anode Support Layer After Redox Cycling

To understand how redox cycling as the result of long term use affects the strength of SFCM based SOFCs, SFCM-GDC ASL test coupons were cycled for 10 times between nitrogen and 10% H<sub>2</sub> environments. Figure 5.7 shows the strength and modulus from the samples which were not cycled (0 cycles) and those cycled 10 times, tested using a four-point bend at ambient conditions. Table 5.3 summaries the means and standard deviations of the test results. The overlapping Student's

Table 5.2: Summary of Weibull fitting parameters (characteristic strength and Weibull modulus) for SFCM-GDC/GDC half-cells at different environments

Temp. (°C)	Environment	Cha.	$\alpha$	$\alpha$	Weibull	$\beta$	$\beta$
		Strength ( $\alpha$ , MPa)	Lower CI	Upper CI	Modulus ( $\beta$ )	Lower CI	Upper CI
20	Air	60.6	57.4	63.6	10.4	6.89	14.7
600	Hydrogen	42.5	39.2	45.8	7.29	4.79	10.3

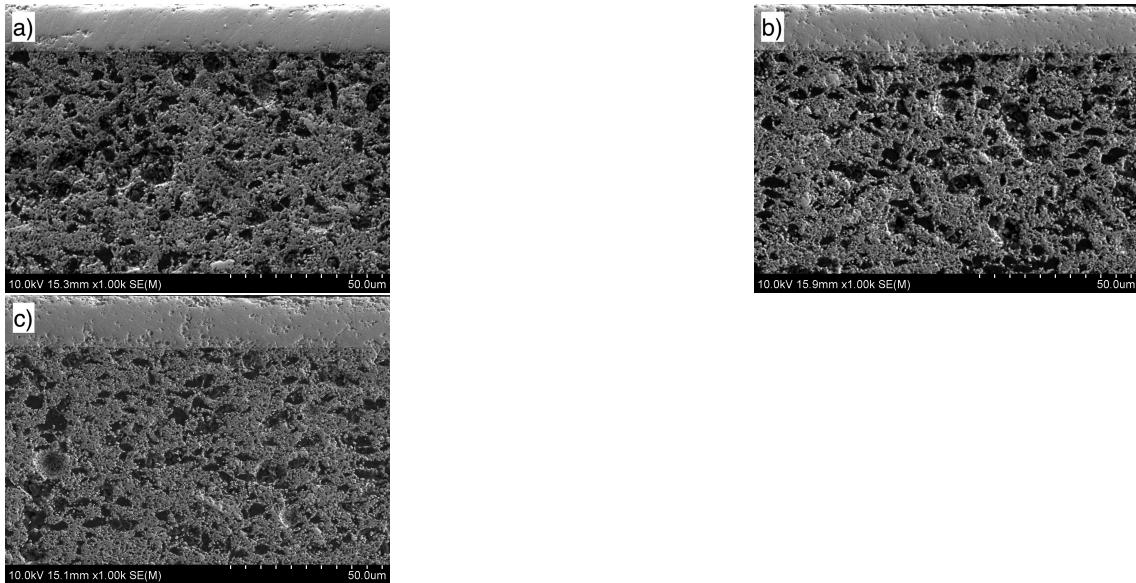


Figure 5.6: Scanning electron microscope images of epoxy filled and polished SFCM-GDC/GDC half-cell cross sections tested at a) 20 °C in air, b) 600 °C in air and c) 600 °C in 5% H<sub>2</sub>.

Table 5.3: Summary of Cycled SFCM-GDC ASL Mechanical Properties

Number of Cycles		Mean	Modulus	Mean	Strength	
	Number	Number	Modulus	Std Dev	Strength	Std Dev
		(GPa)	(GPa)	(MPa)	(MPa)	
0	14	24.5	5.01	34.3	7.23	
10	20	27.3	3.60	22.4	4.94	

t circles in Figure 5.7b demonstrate that cycling did not significantly change the elastic modulus of the samples, while the strength did significantly decrease. This is the result of changes in microstructural flaws, rather than the change of an intrinsic material property.

The strengths of the cycled and un-cycled cells were fitted to Weibull distributions to observe how flaw distributions changed with redox cycling. Figure 5.8 presents the fitted data and distributions and Table 5.4 summarizes the fit parameters of the Weibull modulus with 95% confidence intervals. The Weibull moduli between the two data sets are very similar, indicating that the flaw distribution is the same between them. The decrease in characteristic strength is then due to the growth of flaws with cycling. SEM images in Figure 5.9 are of a sample which had not been cycled (a) and one which had been cycled 10 times (b) after being epoxy filled and polished. The sample which had been cycled 10 times has a greater number of pores at larger sizes compared to the un-cycled sample. This indicates that the finer microstructure of the pores is susceptible to changes during redox cycling due to chemical expansion, but the larger flaws which lead to complete cell failure do not

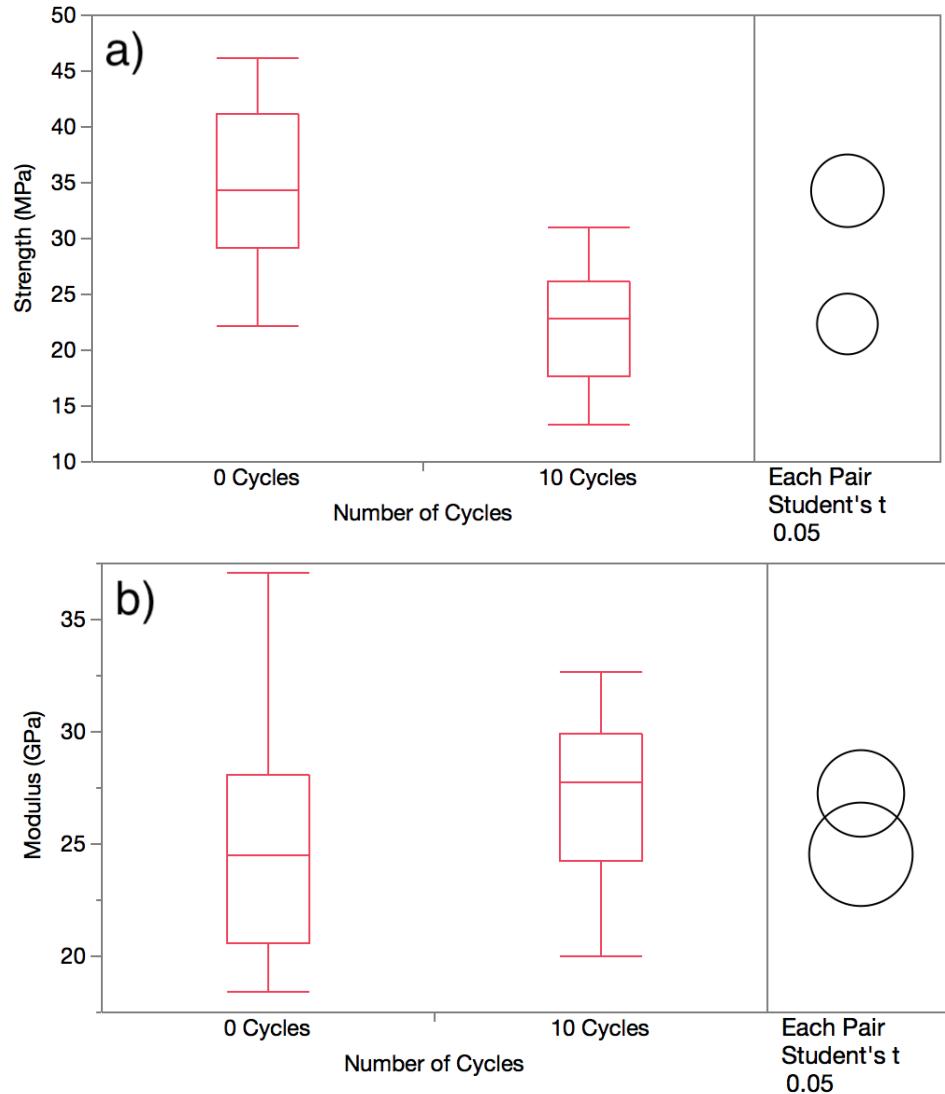


Figure 5.7: Results of four point bend test at ambient conditions of SFCM-GDC ASL with a) strength and b) modulus for samples before any cycling and after 10 redox cycles between 10% H<sub>2</sub> and N<sub>2</sub>.

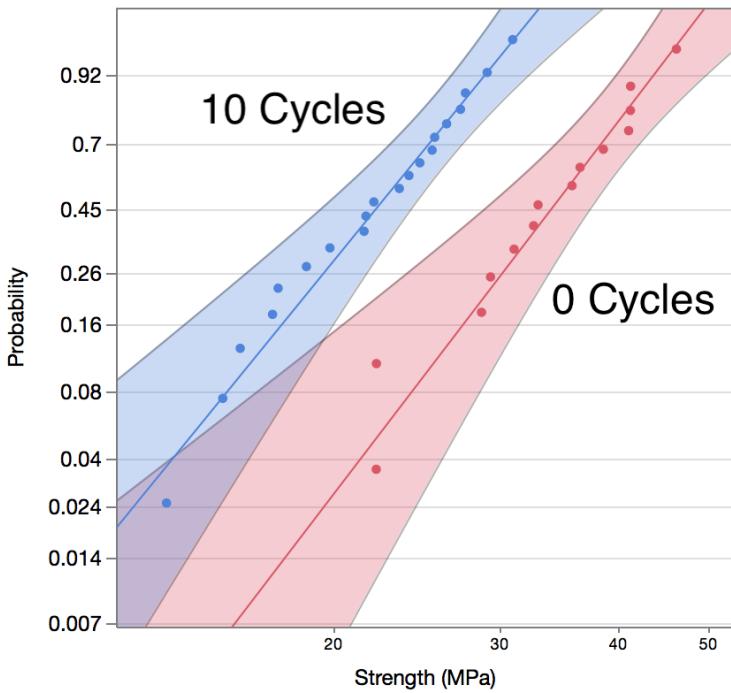


Figure 5.8: Fitted Weibull distributions of SFCM-GDC ASL before any cycling and after 10 redox cycles between 10% H<sub>2</sub> and N<sub>2</sub>, plotted linearly with 95% confidence intervals shaded

change as the result of redox cycling. [60]

## 5.4 Conclusions

In this work the mechanical properties of SFCM and SFCM-GDC structures are characterized as the environment is changed from ambient to the working conditions of SOFCs and with redox cycling. The electrical conductivity of SFCM-GDC is stable up to 19 cycles due to the reversibility and phase stability of SFCM-GDC in the environment range. The fracture toughness of SFCM was found to be  $(0.124 \pm 0.023) \text{ MPa}\sqrt{\text{m}}$  at room temperature and increases with temperature, due

Table 5.4: Summary of Weibull Fit Parameters (characteristic strength and Weibull modulus) for Cycled SFCM-GDC ASL

Number of Cycles	Char. Strength ( $\alpha$ , MPa)	$\alpha$	$\alpha$	Weibull Modulus ( $\beta$ )		$\beta$	CI Lower CI Upper
		CI Lower	CI Upper	CI Lower	CI Upper		
0	37.1	33.7	40.8	5.75	4.06	9.85	
10	24.3	22.3	26.5	5.39	4.00	8.28	

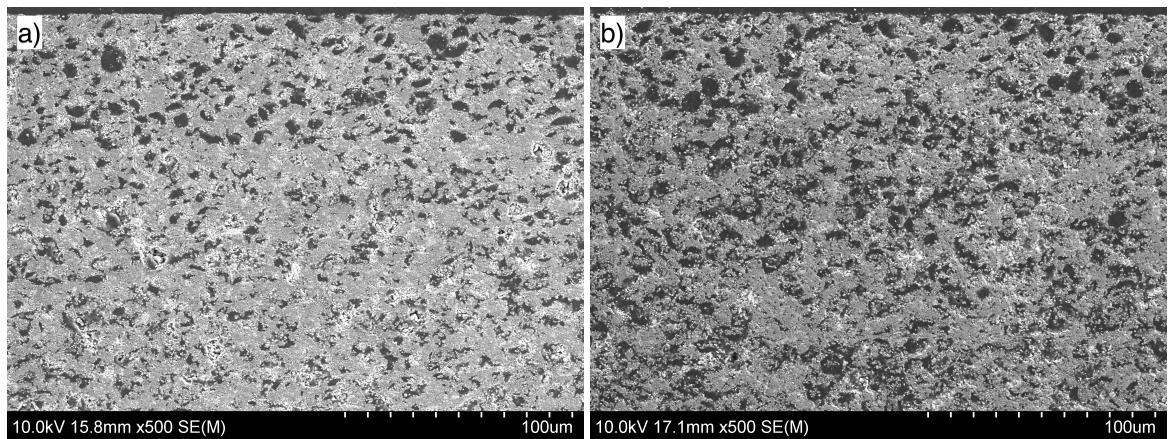


Figure 5.9: Scanning electron microscope images of epoxy filled and polished SFCM-GDC ASL cross sections tested a) before any cycling, b) after 10 cycles between 10%  $H_2$  and  $N_2$ .

to relaxation of residual stresses. The flexural strength of SFCM-GDC/GDC half-cells increases by 23.9% upon heating from room temperature to 600 °C. This is due to thermal expansion pushing cracks closed during heating, requiring additional stress to propagate surface cracks and the increase in fracture toughness. Once exposed to reducing conditions, the flexural strength decreases by 29.4% of the original strength, as SFCM and GDC generate oxygen vacancies. Reduction was shown to increase the size and variability of the distribution of flaws which lead to failure. Redox cycling led to the uniform increase in critical flaw size and changed the fine microstructural porosity, decreasing strength from 34.3 MPa to 22.4 MPa.

These findings show that SFCM, when combined with GDC, make a suitable anode material for SOFCs. SFCM-GDC is a stable material system, both in terms of conductivity and mechanically, with redox cycling. Reduction does increase the likelihood of failure by decreasing characteristic strength and the distribution of flaws, but repeated cycling only decreases characteristic strength and does not change the Weibull modulus.

## Chapter 6: Conclusions

### 6.1 Solid-Oxide Fuel Cells

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## Appendix A: Statistics

### A.1 Student's t-test

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## A.2 Weibull Statistics

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## Appendix B: TGA Manual

### B.1 Theory of Operation

Thermogravimetry works on the principle of measuring small changes in mass as the environment changes. Changes in environment can come from

### B.2 Mass Measurement

The TGA uses a Cahn D200 microbalance for the mass sensing capability.

### B.3 Gas Delivery

MKS Controllers are used.

### B.4 pO<sub>2</sub> Measurement

Home built YSZ sensor.

### B.5 Controls

Lab view on the computer.

## B.6 Interfacing with other devices

Can be plumbed up to mass spec.

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## Appendix C: Code

### C.1 Arduino PID Relay Furnace Controller with Serial Connectivity

The purpose of this Arduino sketch is to power a heating furnace (controlled by a relay), with PID controls. In addition serial communications are added to monitor, log, and interact with the controller.

#### C.1.1 Hardware and other libraries

This was built to be used on a Arduino Uno R3, but should be easily run on a variety of different boards. For temperature sensing, an [Adafruit MAX31856](#) is used with the [library](#) from them. Also used is the PID controller [library by br3ttb](#). All I have really done is put the two together with the ability to communicate over serial.

#### C.1.2 Variables

Here are a list of variables for things you may want to change based on your setup.

- RelayPin: The physical pin your relay is connected to.
- Adafruit\_MAX31856(CS, DI, DO, CLK): Pins for your MAX31856

- WindowSize: Length of on/off cycle, needed to account for AC power
- printdelay: Delay time in milliseconds for printout on serial
- MaxOP: Maximum operating power, used to extend life of elements
- myPID(&Input, &Output, &workingSet,P,I,D, DIRECT): PID need to be adjusted for your setup. If inverse behavior is experienced (e.g. heats when it should cool) switch DIRECT.
- workingSet and Setpoint: Initial setpoint for power on
- ramrate: Sets a ramp rate for the working setpoint. Measured in milliseconds for 1C change.

### C.1.3 Serial communications

Baud rate is set to 9600. Output is tab delimited of Setpoint, Working Setpoint, Thermocouple Temperature, and Output Power. To change set point, send a new number over serial and press return. You may have to adjust your serial monitor to send \n as end of line.

```

1 #include <Adafruit_MAX31856.h> //loads library for thermocouple reader
2 #include <PID_v1.h> //loads PID library
3 #include <RunningAverage.h> //loads class for Running Average
   ↵ calculations
4 #define RelayPin 2 //set pin number which is connected to power relay
   ↵ for device
5

```

```

6 const byte numChars = 32;

7 char receivedChars[numChars]; // an array to store the received data

8

9 boolean newData = false; //trigger to determine if data needs to be
    ↪ read

10

11 Adafruit_MAX31856 max = Adafruit_MAX31856(4, 5, 6, 7); // Software SPI,
    ↪ Pin number for: CS, DI, DO, CLK

12

13 //Define Variables

14 double workingSet, Setpoint, Input, Output;

15 int WindowSize = 1000; //Length of cycle for power on/off

16 unsigned long prevprintMillis = 0;

17 const long printdelay = 5000; //delay amount before printing via serial

18 unsigned long windowStartTime;

19 unsigned long prevRampTimer = 0;

20 unsigned long MaxOP = .95; // Max Operating Power

21

22 RunningAverage myRA(10); //Set up running average with # of
    ↪ measurements

23

24 PID myPID(&Input, &Output, &workingSet, 250, 50, 8, DIRECT); //Specify the
    ↪ links and initial tuning parameters

25

26 void setup() {
27     pinMode(RelayPin, OUTPUT); //define RelayPin as an output
28

```

```

29 //staring serial communications
30 Serial.begin(9600);
31 Serial.println("PID Controller Output");
32 Serial.println("Setpoint\t Working SP\t TC Temp\t Output");//tab
   ↪ delimited for logging
33
34 //setup for thermocouple reader
35 max.begin();
36 max.setThermocoupleType(MAX31856_TCTYPE_K);//change type if needed
37
38 windowStartTime = millis(); //start timer for duty cycle window
39
40 myRA.clear(); // explicitly start clean
41
42 //initialize the variables we're linked to
43 workingSet = 20;
44 Setpoint = 20;
45
46 myPID.SetOutputLimits(0, MaxOP * WindowSize); //tell the PID to range
   ↪ between 0 and the full window size
47 myPID.SetMode(AUTOMATIC); //turn the PID on
48
49 }
50
51 //fuction to recieve data via serial and process when endmarker is
   ↪ received
52 void recvWithEndMarker() {

```

```

53 static byte ndx = 0;
54
55 char rc;
56
57 // if (Serial.available() > 0) {
58
58 while (Serial.available() > 0 && newData == false) {
59
60     rc = Serial.read();
61
62     if (rc != endMarker) {
63
64         receivedChars[ndx] = rc;
65
66         ndx++;
67
68     if (ndx >= numChars) {
69
70         ndx = numChars - 1;
71
72     }
73
74 } //}
75
76 //Function to repeat new setpoint for confirmation
77 void showNewData() {
78
78 if (newData == true) {
79
80     String recievedString = String(receivedChars);

```

```

80 Serial.print("Setpoint changed to ... ");
81 Serial.println(recievedString.toFloat());
82 Setpoint = recievedString.toFloat();
83 newData = false;
84 }
85 }
86
87 void loop() {
88 recvWithEndMarker(); //check for new setpoint
89 showNewData(); //sets new setpoint and displays it
90
91 // Input = max.readThermocoupleTemperature(); //read thermocouple
92
93 myRA.addValue(max.readThermocoupleTemperature());
94
95 Input = myRA.getAverage();
96
97 myPID.Compute(); //calculate PID output
98
99 //print delay for serial output so not to flood logs
100 unsigned long printMillis = millis();
101 if (printMillis - prevprintMillis >= printdelay) {
102     prevprintMillis = printMillis;
103     Serial.print(Setpoint); Serial.print("\t"); Serial.print(workingSet);
104     → Serial.print("\t"); Serial.print(max.readThermocoupleTemperature
105     → ()); Serial.print("\t"); Serial.println(Output/WindowSize*100);
106 }

```

```

105
106 //turn the output pin on/off based on pid output
107 if( millis() - windowStartTime>=WindowSize)
108 { //time to shift the Relay Window
109     windowStartTime += WindowSize;
110 }
111 if( Output < millis() - windowStartTime) digitalWrite(RelayPin,LOW); //  

    ↳ HIGH and LOW set to default off
112 else digitalWrite(RelayPin,HIGH);
113
114 //sets ramp rate functionality
115 unsigned long ramptimer = millis();
116 unsigned long ramprate = 6000;//milliseconds for 1C change
117 if( workingSet != Setpoint)
118 {
119     if( ramptimer - prevRampTimer >= ramprate && workingSet < Setpoint)
120     {
121         workingSet++;
122         prevRampTimer = ramptimer;
123     }
124     if( ramptimer - prevRampTimer >= ramprate && workingSet > Setpoint)
125     {
126         workingSet--;
127         prevRampTimer = ramptimer;
128     }
129 }
130 }
```

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